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CO_2 + Methanol + Glycerol: Multiphase behaviour

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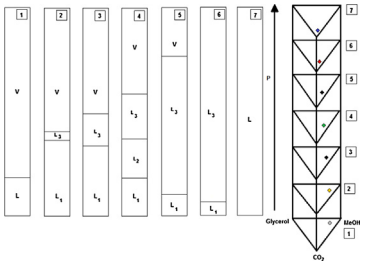
GRAPHICAL ABSTRACT

Graphical representation of the multiphase behaviour of the system CO2 + Methanol + Glycerol with stepwise addition of CO2 to a 4 cm3 liquid mixture of methanol and glycerol at molar ratio of 30 and 313 K.



ABSTRACT

The phase behaviour of the system CO_2 + methanol + glycerol has been studied at low concentrations of this tri-alcohol. The synthetic method was implemented in a visual sapphire cell. New phase diagrams were obtained at temperatures of 313.15 and 333.15 K. Different methanol/glycerol molar ratios of 113, 50 and 30 were considered and its influence on phase behaviour accounted for. Pressures were varied from 6.03 to 11.44 MPa. A specific experiment is reported, starting from an initial volume of 4 mL of liquid mixture methanol + glycerol (methanol/glycerol molar ratio 30), where, with a stepwise addition of CO_2, diverse fluid phase phenomena were detected, such as VLE, Critical Point, VLLE, VLLLE, LLE and LE.

1. Introduction

The reaction of CO_2 and glycerol to obtain glycerol carbonate has been intensively studied, nevertheless with scarce results, due to several adverse factors, including a very low mutual solubility of the reactants and a small equilibrium constant of the reaction [1,2]. Attempts to carry out the reaction with both reactants dissolved in methanol have uncovered the potential impact of the complex phase behaviour of the methanol + CO_2 + glycerol system on the reaction yields [3].

Pinto et al. [4] studied the fluid phase equilibria of those mixtures. Complex fluid phase phenomena, such as three-phase vapour-liquid-liquid (VLLE) equilibrium and liquid-liquid (LLE) immiscibility at higher pressures, were reported. Diverse studies were carried out in this context for mixtures of CO_2 + water + a low chain alcohol, ethane or ethane + water + 1-propanol, and CHF_3 + water + 1-propanol [5–7]. In those studies multiphase behaviour has been detected, including four phase equilibria (VLLLE). In a case study relevant for the present work [6], the domains of existence, in the pressure-temperature space, of these equilibria were carefully measured and a complex picture emerged.

The results of Pinto et al. referred to above could be qualitatively interpreted on the basis of this picture, if we hypothesise that the

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